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APPLICATIONS OF GC/MS/MS FOR THE ULTRA-TRACE DETERMINATION OF CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS IN COMPLEX ENVIRONMENTAL SAMPLES

E.J. REINER, D.H. SCHELLENBERG, V.Y. TAGUCHI,
D.M. McCURVIN AND R.E. CLEMENT
ONTARIO MINISTRY OF THE ENVIRONMENT
REXDALE, ONTARIO, M9W 5L1, CANADA

The analysis of chlorinated dibenzo-p-dioxins (CDD) and dibenzofurans (CDF) in complex matrices, which oftentimes contain chemical interferences at concentrations several orders of magnitude greater than those of the CDD and CDF, requires extensive sample cleanup prior to instrumental analysis. Limitations in sample cleanup place additional demands on the instrumentation.

The difficulties in the analysis of environmental samples make selectivity and sensitivity important considerations for the method of choice. Capillary column high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS) has been the standard method for analyzing CDD and CDF in complex matrices such as sediments, effluents and biological tissues.

Single reaction monitoring (SRM) on tandem mass spectrometers can also be used to achieve the enhanced selectivity and corresponding sensitivity required for the analysis of CDD and CDD in complex matrices. The signal strength of the daughter or progeny ions in SRM are strongly dependent on a number of parameters, such as: collision gas pressure, collision energy, electron energy, nature of the collision gas, the energy of Q_3 relative to Q_2, the design of the collision cell and the type of the detector. In order to maximize the signal strength of the progeny ions, these parameters must be optimized.

Until recently, tandem mass spectrometry (MS/MS) has been able to meet the requirements for selectivity but has been approximately one order of magnitude less sensitive than HRGC/HRMS methods. Optimization of tuning parameters using 1 ug of the analyte of interest in a direct insertion probe (DIP) [1] rather than PFTBA resulted in sensitivities comparable to the HRGC/HRMS technique reported previously [2]. Table 1: compares the limits of detection, reported in 1986, by three manufacturers of triple quadrupole mass spectrometers, using PFTBA or PFK for tuning, to the limits of detection that were obtained when dioxins and furans were used for tuning and to limits of detection obtained by HRMS. Most of the limits of detection obtained by the MS/MS dioxin tune method are between one and two orders of magnitude lower than when PFTBA or PFK is used for tuning and almost as low as those obtained by HRMS.

Collision induced dissociation breakdown graphs were used initially to optimize parameters such as collision energy and

collision gas pressure. The breakdown graphs for PFTBA, 2,3,7,8-Cl_4DD and 2,3,7,8-Cl_4DF plotted vs. collision gas pressure are shown in Figure 1. The optimum collision gas pressure for the dioxin and furan was 3.3 mtorr while that for PFTBA was 0.7 mtorr. Figure 2: shows the breakdown graphs of PFTBA and four Cl_4DD congeners. The optimum collision energy for PFTBA was 25 eV while those for the dioxins were between 20 and 28 eV. The variation in optimum collision energy for the four Cl_4DD congeners implies that the relative response factors within a congener group are dependent on collision energy. Figure 3: shows the mass chromatogram of a mixture of three Cl_4DD congeners (1,2,3,4-, 2,3,7,8-, and 1,2,7,8-). Injection A was run with parameters set to optimize 2,3,7,8-Cl_4DD while injection B was set to optimize 1,2,3,4-Cl_4DD. As expected, the signal strength of 2,3,7,8-Cl_4DD was enhanced in injection A and the signal strength of 1,2,3,4-Cl_4DD was enhanced in injection B. In order to obtain reproducible relative response factors, a 2,3,7,8-containing (the most toxic) congener was chosen for each group. These are shown in Table 2.

Each probe sample was prepared by evaporating 1 ug standards of a furan and the corresponding dioxin with the same number of chlorines in the same sample cup. Each of the five cups (Cl_4DF/DD to Cl_8DF/DD) was inserted in turn into the mass spectrometer using the DIP and parameters such as collision gas pressure, collision energy, electron energy, lens voltages, quad offsets, etc. were optimized for both the furan and dioxin.

Another factor that increased the signal strength of the dioxins and furans was elevation of the source temperature to 250°C. This enhanced the signal strength of the congeners of higher chlorine substitution. Also, a high trap current (300 uA) and a Finnigan 4500 ion volume instead of the normal TSQ-70 ion volume was used to increase the flux of the ionizing electrons into the ion source.

The advantages obtained by using the dioxin tune method include: good sensitivity - less than 1 picogram of dioxins and furans can be detected for all congeners; infrequent tuning - about 3 to 4 times a year @ 200 injections / month with source and rod cleaning every six months (ion volumes are changed daily); and selectivity - the reduced chemical noise gives an increase in the S/N ratio and therefore an enhancement in sensitivity over single quadrupole instruments.

Example 1 shows the mass chromatogram of a 500 fg standard injected on a 30m SE-52 capillary column with a split/splitless injector. Note the signal to noise is about 10:1. Example 2 shows 2pg of 2,3,7,8-Cl_4DD in a fish extract injected on the same column using the "DOW" only cleanup. This sample was injected about 3 weeks after the last time the instrument was optimized (tuned). Example 3 shows a comparison of a fish extract (Dow only cleanup) run on both a ZAB-2F and TSQ-70 mass spectrometer. Note that the chromatogram of the sample determined by MS/MS is much cleaner than that determined by HRMS at 12,000RP. Example 4 shows the mass chromatograms of an effluent sample. Note that the relative response factors obtained in the GC/MS/MS mode, when 2,3,7,8- dioxins and furans are used for tuning, are very similar to those obtained in the GC/MS mode. This indicates that the

the total concentration determination for a congener group would be similar in both the GC/MS and GC/MS/MS modes.

1. Schellenberg D.H. et al, Rapid Comm. in Mass Spectrom., 1,111,(1987).
2. Taguchi V.Y. et al, Anal. Chem., 60, 1429, (1988).

TABLE 1: MOE MS/MS COMPARISON LIMIT OF DETECTION

CONGENER	MANUFACTURER A	B	C	PRESENT METHOD	HRMS[1]
Cl_4DD	2	2	8	0.3	0.2
Cl_5DD	5	4	9	0.5	0.2
Cl_6DD	10	10	23	0.3	0.2
Cl_7DD	15	15	19	0.3	0.2
Cl_8DD	20	25	38	0.6	0.4
Cl_4DF	4	3	7	0.3	0.2
Cl_5DF	5	4	11	0.3	0.2
Cl_6DF	10	8	21	0.2	0.2
Cl_7DF	15	10	20	0.5	0.2
Cl_8DF	20	20	19	0.5	0.2

ALL DATA IN PICOGRAMS

TABLE 2: Congeners Used for Tuning in MS / MS

2,3,7,8-Cl_4DD
1,2,3,7,8-Cl_5DD
1,2,3,4,7,8-Cl_6DD
1,2,3,4,6,7,8-Cl_7DD
Cl_8DD

2,3,7,8-Cl_4DF
1,2,3,7,8-Cl_5DF
1,2,3,4,7,8-Cl_6DF
1,2,3,4,6,7,8-Cl_7DF
Cl_8DF

FIGURE 1 : COLLISION GAS PRESSURE BREAKDOWN GRAPHS

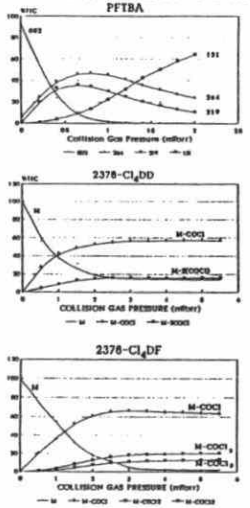


FIGURE 2 : COLLISION ENERGY BREAKDOWN GRAPHS

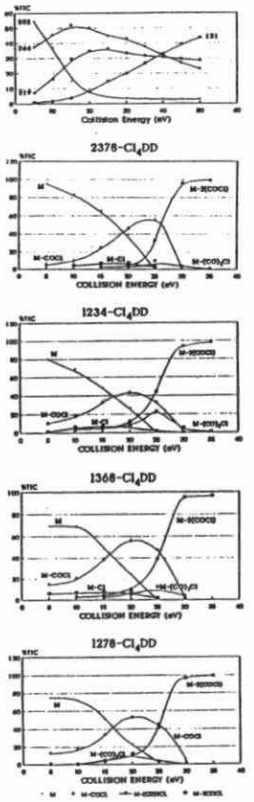
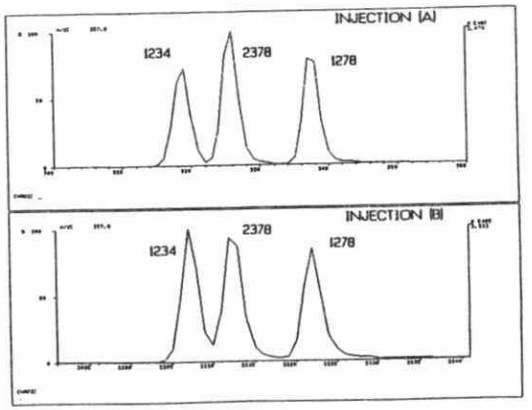
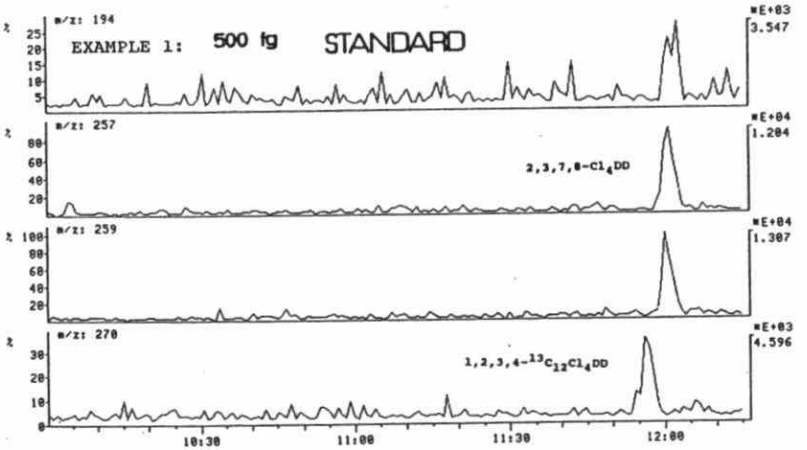
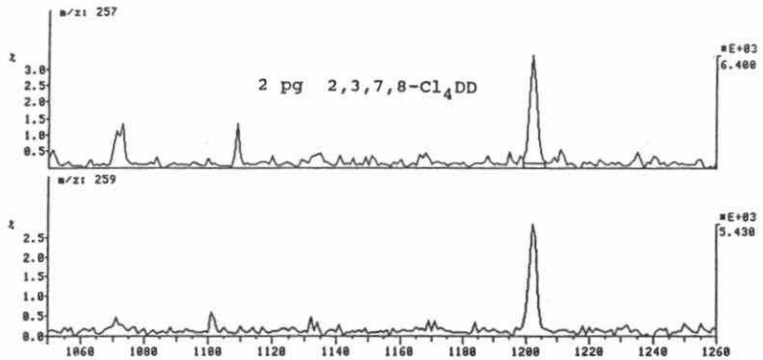


FIGURE 3 : Cl_4DD STANDARDS (100pg)



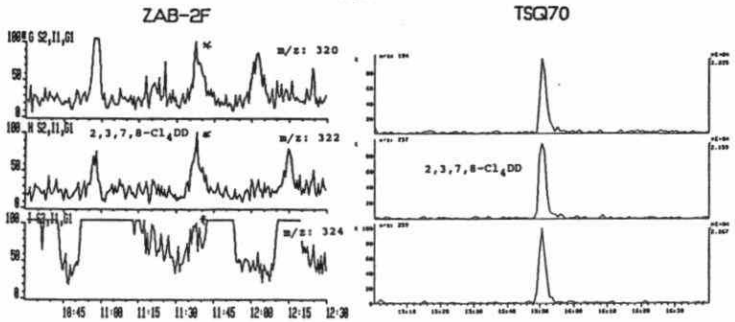


EXAMPLE 2: FISH



EXAMPLE 3:

FISH



EXAMPLE 4: COMPARISON OF RELATIVE RESPONSE FACTORS